

PTO 01-1624

German
Document No. WO 99/04750

USE OF POLYMERS CONTAINING POLYSILOXANE FOR COSMETIC FORMULATIONS
[Verwendung von Polysiloxanhaltigen Polymeren für Kosmetische
Formulierungen]

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UNITED STATES PATENT AND TRADEMARK OFFICE
Washington, D.C. March 2001

Translated by: Schreiber Translations, Inc.

<u>Country</u>	:	Europe
<u>Document No.</u>	:	WO 99/04750
<u>Document Type</u>	:	Patent Application
<u>Language</u>	:	German
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<u>IPC</u>	:	A61K 7/00
<u>Application Date</u>	:	July 20, 1998
<u>Publication Date</u>	:	February 4, 1999
<u>Foreign Language Title</u>	:	Verwendung von Polysiloxanhaltigen Polymeren für Kosmetische Formulierungen
<u>English Language Title</u>	:	USE OF POLYMERS CONTAINING POLYSILOXANE FOR COSMETIC FORMULATIONS.

Specification

Synthetic polymers have been used successfully for almost 50 years to strengthen hairdos. Initially, preference was given to vinyl lactam-homo and copolymers for practical use; later on, carboxylate-group-containing polymers gained increasing importance. The desired property profile, such as intensive strengthening at high air humidity, elasticity, ability to wash out of the hair, and compatibility with the other formulation components can be achieved by copolymerization of a combination of hydrophobic, elastifying and carboxyl-group-containing monomers.

Nowadays, the above-mentioned requirements can be met by various types of polymers; nevertheless, the grip of hairdos strengthened with these polymers is increasingly felt as being unpleasantly dull and "unnatural." Attempts to improve the situation by means of additions to the formulations so far have not led to entirely satisfactory results: the addition of the usual softening agents does improve the hold but at the same time it reduces the strengthening effect in many cases. The polysiloxanes that are used frequently are not compatible with the polar polymers and often require further additions before they can be formulated at all. Unmixing can lead to problems

¹Numbers in the margin indicate pagination in the foreign text.

during the settlement of the formulation and during actual use.

There have therefore been many attempts to bind polysiloxane groups to the strengthening polymer in a covalent manner to prevent any unmixing. By way of example, European Patent EP 0408311 describes hair care polymers consisting of a monomer that contains polysiloxane groups and the customary hydrophile and hydrophobic monomers. European Patent Applications EP 0412704 and EP 0412707 propose that polysiloxane groups, in the form of macromonomers, with molar masses of 1,000 to 50,000, the polymerize with the usual hydrophobic and hydrophile monomers. The synthesis of these monomers is extraordinarily laborious. One can hardly separate - from the polymers - any macromonomers that are not mixed, as well as their non-reactive impurities, on account of their high molecular weight. They represent a toxicological and allergenic risk. Moreover, the resultant copolymers - to achieve a good effect - often can be formulated only in combination with other polymers, carriers, and other aids, such as taught by the above-mentioned patents. /2

DE 42 40 108 describes polysiloxanes-containing bonding agents that are suitable dirt-repellent coatings, in particular, as anti-graffiti coatings. But these bonding agents are paint-like and are not suitable for cosmetic purposes.

DE 16 45 569 describes a process for the production of silicon-organic graft mixed polymers and their use as foam

masses.

The object of the invention is to provide polymers for hair cosmetics without the disadvantages described here.

The discovery relates to the use of polymers, that are water-soluble or water-dispersable or that -- if they consist of monomers with neutrilizable residues -- are water-soluble or water-dispersable in a neutralized form which can be obtained in the following manner:

- (a) Ethylenically unsaturated monomers in the presence of
 - (b) polyalkyleneoxide-containing silicon derivatives,
- that are radically polymerized, for cosmetic formulations.

By the term "water-dispersable" in the context of this invention, we mean polymers that, in contact with water, within 24 hours, form a fluid that, without any optical aids, with the naked eye, will not reveal any solid particles. To check whether a polymer is water-dispersable, one puts 100 mg of the polymer, in the form of a 100-micron m thick film, in 100 ml of water (20° C) and one shakes it for 24 hours on a commercially available shaker table. If, after shaking, no solid particles can be recognized any longer, but if the fluid is clouded, then the polymer is water-dispersable; without clouding, it is labeled as water-soluble.

If the silicon compounds are not present during polymerization, but if they are mixed in after polymerization,

then as a rule one gets very soft, sticky films that are unsuitable for the invention-based uses in hair cosmetics (see comparison examples 8 and 24).

This would indicate that, during polymerization, there is possibly a grafting of the polymerides upon the silicon compounds, and this contributes to good film properties, such as no stickiness, high surface smoothness, and hardness. But one can also visualize mechanisms other than grafting by means of which the invention-based polymers can develop their advantageous properties. /3

As suitable polymerizable monomers (a), one can preferably employ Ethylenically unsaturated monomers. In the process, one can use either an individual monomer or a combination of two or more monomers. By "polymerizable" we mean here that the monomers used can be polymerized by employing any kind of conventional synthetic method.

By way of example, this could involve solution polymerization, emulsion polymerization, reverse emulsion polymerization, suspension polymerization, reverse suspension polymerization or precipitation polymerization, although the usual methods are not confined to that. In the case of solution polymerization, one can use water, customary organic solvents, or the invention-based silicon derivatives, themselves, as solvents.

Monomers that can be polymerized with a reaction initiated

by free radicals are preferred. The term "ethylenically unsaturated" means that the monomers have at least one polymerizable carbon-carbon double bond that can be mono-, di-, tri-, or tetra-substituted.

The monomers (a) of the polysiloxane-containing polymers of this invention can account to 50 to 99.9% by weight, preferably 70 to 99% by weight, particularly preferably 85 to 98% by weight.

The preferred ethylenically unsaturated monomers (a) can be described by the following general formula:



where

X is chosen from the group of -OH, OM, OR⁸, NH², NHR⁸, N(R⁸)₂ residues;

M is a cation, chosen from the group consisting of the following Na⁺, K⁺, Mg⁺⁺, Ca⁺⁺, Zn, NH₄⁺, alkylammonium, dialkylammonium, trialkylammonium and tetraalkylammonium;

the R⁸n residues can be chosen identically or different, from the group consisting of -H, C₁-C₄₀ linear or branched-chain alkylresidues, N,M-dimethylaminoethyl, 2-hydroxyethyl, 2-methoxyethyl, 2-ethoxyethyl, hydroxypropyl, methoxypropyl, ethoxypropyl.

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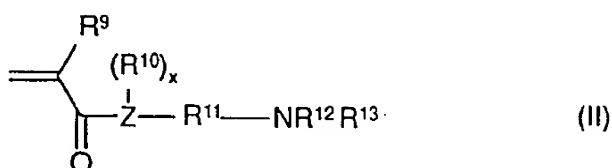
R⁷ and R⁶ are chosen independently of each other from the group consisting of -H, C₁-C₈ linear - branched-alkyl chains, methoxy, ethoxy, 2-hydroxyethoxy, 2-methoxyethoxy and 2-

ethoxyethyl.

Representative but not restrictive examples of suitable monomers (a) are, for instance, acrylic acid and its salts, esters, and amides. The salts can be derived from any desired non-toxic metal, ammonia, or substituted ammonium-counter ions.

The esters can be derived from C₁-C₄₀ branched-chain or C₃-C₄₀ carbocyclic alcohols, from multifunctional alcohols with 2 to about 8 hydroxyl groups, such as ethyleneglycol, hexylenglycol, glycerin, and 1,2,6-hexanetriol, from amino alcohols or from alcohol ethyls, such as ethoxyethanol or polyethylene glycols.

Also suitable are N,N-Dialkylaminoalkylacrylate and methacrylate and N-dialkylaminoalkylacryl- and -methacrylamide, having the general formula (II).



where R⁹=H, alkyl with 1 to 8 C-atoms

R¹⁰=H, methyl,

R¹¹= alkylene, with 1 to 24 C-atoms, optionally substituted with alkyl,

R¹², R¹³= C₁-C₄₀ alkyl residue,

Z= nitrogen when x=1 or oxygen when x=0

The amides can be unsubstituted, N-alkyl or N-alkyl amino

mono-substituted or N,N-dialkylsubstituted or N,N-dialkylamino disubstituted, wherein the alkyl or alkyl amino-groups are derived from C1-C40 linear, C3-C4 branched-chain, or C3-C40 carbocyclic units. In addition, the alkyl amino groups can be quaternized. /5

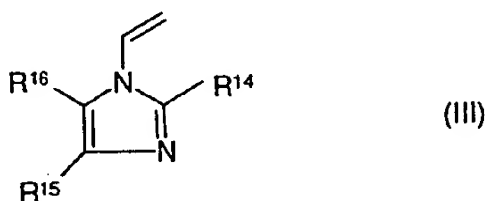
Preferred monomers having formula II are N,N-dimethylaminoethyl-(meth)acrylate, N,N-dimethylaminoethyl(meth)acrylate, N,N-dimethyl(meth)acrylate.

Also usable monomers (a) are substituted acrylic acids as well as salts, esters, and amides thereof; the substituents on the carbon atoms are in the two or three position of acrylic acid and are chosen independently of each other from the group consisting of C1-C4 alkyl, CN, COOH, particularly preferred here being methylacrylic acid, ethacrylic acid and 3-cyanoacrylic. These salts, esters, and amides of these substituted acrylic acids can be chosen, as described above for the salts, esters, and amides of acrylic acid.

Other suitable (a) monomers are vinyl- and allyl esters of C1-C40 linear, C3-C40 branch-chain, or C3-C40 carbocyclic acids (for instance: vinyl acetate, vinylpropionate, vinylneonanoate, vinylneoundecanic acid or t-butyl-benzoic acid-vinylester); vinyl-or allylhalogenides, preferably vinylchloride and dodecylvinylether, vinylformamid, vinylmethylacetamide, vinylamine; vinyl lactames, preferably vinylpyrrolidione and

vinylcaprolactam, vinyl- or allyl-substituted heterocyclic compounds, preferably vinyl pyridine, vinyloxazoline and allyl pyridine.

Also suitable are N-vinylimidazols having the general formula III, where R^{14} to R^{16} , independently of each other, stand for hydrogen, C_1 - C_4 -alkyl or phenyl:



other suitable (a) monomers are diallylamines having the general formula (IV)



where $R^{16}=C_1$ to C_{24} alkyl

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other suitable (a) monomers are vinylidenechloride; and hydrocarbons with at least carbon-carbon double bond, preferably styrene, alpha-methylstyrene, tert. - butylstyrene, butadiene, isoprene, cyclohexadiene, ethylene, propylene, 1-butene, 2-butene, isobutylene, vinyltoluene, as well as mixtures of these monomers.

Particularly suitable (a) monomers are acrylic acid,

methylacrylic acid, ethylacrylic acid, methylacrylate,
 ethylacrylate, propylacrylate, n-butylacrylate, iso-
 butylacrylate, t-butylacrylate, 2-ethylhexylacrylate,
 decylacrylate, methyl methacrylate, ethyl methacrylate,
 propylmethacrylate, n-buty methacrylate, iso-buty methacrylate, t-
 buty methacrylate, 2-ethylhexylmethacrylate, decylmethacrylate,
 methylethacrylate, ethylethacrylate, n-butylethacrylate, iso-
 butylethacrylate, t-butyl-ethacrylate, 2-ethylhexylmethacrylate,
 decylmethacrylate, 2,3-dihydroxypropylacrylate, 2,3-
 dihydroxypropylmethacrylate, 2-hydroxyethylacrylate,
 hydroxypropylacrylates, 2-hydroxyethylmethacrylate, 2-
 hydroxyethylmethacrylate, 2-methoxyethylethacrylate, 2-
 ethoxyethylmethacrylate, 2-ethoxyethylmethacrylate,
 hydroxypropylmethacrylates, glycerylmonoacrylate,
 glycerylmonomethacrylate, polyalkylene glycol(meth)acrylates,
 unsaturated sulfonic acids, such as, for instance
 acrylamidopropanesulfonic acid;
 acrylamide, methacrylamide, ethacrylamide, N-methylacrylamide,
 N,N-dimethylacrylamide, N-ethylacrylamide, N-isopropylacrylamide,
 N-butylacrylamide, N-t-butylacrylamide, N-octylacrylamide, N-t-
 octylacrylamide, N-octadecylacrylamide, N-phenylacrylamide, n-
 methylmethacrylamide, N-ethylmethacrylamide, N-
 dodecylmethacrylamide, 1-vinylimidazol, 1-vinyl-2-methylimidazol,
 N,N-dimethylaminoethyl(meth) acrylate, N,Ndiethylaminomethyl(meth

acrylate, N,N-dimethylaminoethyl(meth) acrylate, N,N-dimethylaminododecyl(meth) acrylate, N-[3-(dimethylamino)propyl] methacrylamide, N-[3-(dimethylamino) propyl] acrylamide, N-[3-(dimethylamino) butyl] methacrylamide, N-[8-(dimethylamino) octyl] methacrylamide, N-[12-(dimethylamino) dodecyl] methacrylamide, N-[3-(dimethylamino) propyl] - methacrylamide, N-[3-(dimethylamino) propyl] acrylamide;

maleic acid fumaric acid, maleic acid and hydride, and its semisters, crotonic, itaconic, diallyldimethylamoniumchloride, vinylether (for instance: methyl-, ethyl-, butyl-, or dodecylvinyl- ester), vinylformamide, vinylmethyleacetamide, vinylamine; methyl-vinylketon, maleimide, vinyl pyridine, vinylimidazol, vinylfurance, styrene, styrene -sulfonate, allylalcohol, and mixtures thereof. 17

Among these, the following are particularly preferred: acrylic acid, methylacrylic acid, maleic acid, fumaric acid, crotonic acid, maleic acid and hydride, as well as its semisters, methylacrylate, methyl methacrylate, ethylacrylate, ethyl methacrylate, n-butylacrylate, n-buty methacrylate, t-butylacrylate, t-buty methacrylate, isobutylacrylate, isobutylmethacrylate, 2-ethylhexylacrylate, N-t-butylacrylamide, N-octylacrylamide, 2-hydroxyethylacrylate, hydroxypropylacrylates, 2-hydroxyethylmethacrylate, hydroxypropylmethacrylates, alkylene glycol (meth) acrylate,

unsaturated sulfonic acids, such as, for instance, acrylamidopropane sulfonic acids, vinylpyrrolidione, vinylcaprolactam, vinyl ether (for instance: methyl-, ethyl-, butyl-, or dodecylvinylether), vinyl-formamide, vinylmethylacetamide, vinylamine, 1-vinylimidazol, 1-vinyl-2-methylimidazol, N,N-dimethylaminomethylmethacrylate and N-[3-(dimethylamino) propyl] methacrylamide; 3-methyl-1-vinylimidazoliumchloride, 3-methyl-1-vinylimidazoliummethylsulfate, N,N-dimethylaminomethylmethacrylate, N-[3-(dimethylamino) propyl]- methacrylamide quaternized with methylchloride, methylsulfate or diethylsulfate.

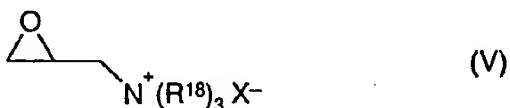
Monomers, with one basic nitrogen atom, can be quaternized in the following manner:

Suitable for the purpose of quaternizing the amines are, for instance, alkylhalogenide with 1 to 24 C-atoms in the alkyl group, for instance, methylchloride, methylbromide, methyliodide, ethylchloride, ethylbromide, propylchloride, hexylchloride, dodecylchloride, lauryl chloride and benzylhalogenides, in particular, benzylchloride and benzylbromide. Other suitable quaternization agents are dialkylsulfate, especially dimethylsulfate or diethylsulfate. The quaternation of the basic amines can also be performed with alkyleneoxides; such as ethyleneoxide or propyleneoxide, in the presence of acids. Preferred quaternation agents are: methylchloride,

dimethylsulfate or diethylsulfate.

Quaternation can be performed prior to polymerization or after polymerization.

Besides, the mixture products of unsaturated acids, such as, for example, acrylic acid or methylacrylic acid, can be employed with a quaternized epichlorohydrin having the general formula (V) ($R^{18} = C\ 1\ to\ C\ 40\ alkyl$). /8



Here are some examples:

(meth)acryloyloxyhydroxypropyltrimethylammoniumchloride and
(meth)acryloyloxyhydroxypropyltrimethylammoniumchloride.

The basic monomers can also be cationized, in that they are neutralized with mineral acids, such as, for instance, sulfuric acid, hydrochloric acid, hydrogen bromide acid, hydriodic acid, phosphoric acid or nitrous acid, or with organic acids, such as, for instance, formic acid, acetic acid, lactic acid, or citric acid.

In addition to the above -mentioned monomers, one can employ, as (a) monomers, so-called macromonomers, such as, for instance, silicon-containing macromonomers with one or several radically polymerizable groups or alkyloxazoline macromonomers, such as they are described, for example, in EP 408 311.

Furthermore, one can employ fluorine-containing monomers, such as they are described, for instance, in EP 558423, compounds that have a cross-linking effect of that regulate the molecular weight, in combination or alone.

As regulators, one can use the compounds that are familiar to the expert, such as, for instance, sulfur compounds for (for instance: mercaptoethanol, 2-ethylhexylthioglycolate, thioglycolic acid or dodecylmercaptan) as well as tribromochloromethane or other compounds that have a regulating effect on the molecular weight of the resultant polymerides.

One can possibly also employ thiol-group-containing silicon compounds.

One preferably employs silicon-free regulators.

As cross-linking monomers, one can use compounds with at least two ethylenically unsaturated double bonds, such as, for instance, esters of ethylenically unsaturated carboxylic acids, such as acrylic acid or methylacrylic acid and multivalent alcohols, ethers of at least bivalent alcohols, such as, for instance, vinylether or allylether. Also suitable are straight-chain or branched, linear or cyclic aliphatic or aromatic hydrocarbons that have at least two double bonds which, in the aliphatic hydrocarbons, must not be conjugate. Also suitable are amines of acrylic and methylacrylic acid and N-allylamines of at least bivalent amines, such as, for instance (1,2-diaminoethane,

1,3-diaminopropane). Also [suitable are] triallylamine or corresponding ammonium salts, N-vinyl compounds of urea derivatives, at least bivalent amides, cyanurates or urethanes. Other suitable cross-linking agents are tetraallylsilane or tetravinylsilane. /9

Particularly preferred cross-linking agents are, for instance, methylenbisacrylamide, triallylamine and trialkylammonium salts, divinylimidazole, N,N'-divinylethylene urea, conversion products of multivalent alcohols with acrylic acid or methylacrylic acid, methylacrylic acid esters and acrylic acid esters of polyalkyleneoxide or multivalent alcohols that have been mixed with ethyleneoxide and/or propyleneoxide and/or epichlorohydrin.

In the polymerization of (a) monomers, one can possibly find present also other polymers, such as, for instance, polyamides, polyurethanes, polyester, homo- and copolymers of ethylenically unsaturated monomers. Examples of such polymers that are partly also used in cosmetics are the polymers used under the following brand Amerhold™, Acronal™, Acudyne™, Stepanhold™, Lovovryl™, Versatyl™, Amphomer™ or Eastma AQ™.

These and other polymers can be admixed to the invention-based polymer preparations also after polymerization.

The invention-based A monomers- provided they provide ionizable groups - can, before or after polymerization, be

neutralized partly or completely with acids or bases in order in this fashion, for example, to adjust the water solubility or dispersibility to a desired measure.

As neutralization agents for acid group-carrying monomers one can employ, for instance, mineral basis, such as sodium carbonate, alkali hydroxides as well as ammonia, organic basis, such as amino alcohols speziell 2-amino-2-methyl-1-propanol, monoethanolamine, diethanolamine, triethanolamine, triisopropanolamine, tri [(2-hydroxy) 1-propyl] amine, 2-amino-2-methyl-1,3-propanediol, 2-amino-2-hydroxymethyl-1,3-propanediol as well as diamines, such as, for instance, lysin.

As neutralization agents for monomers carrying cationizable groups, one may employ, for example, mineral acids, such as hydrochloric acid, sulfuric acid, phosphoric acid, as well as organic acids, such as carboxylic acids, lactic acid, citric acid, or others. /10

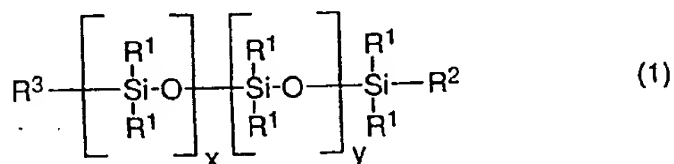
Also present can be processed materials, such as softening agents, film forming agents, pigments, perfumes or others, alone or in combination, during polymerization and/or they can be added after polymerization.

When one uses the invention-based polymers in hair cosmetics, especially when they are used as strengthening agents, it is advantageous to set the glass temperature of the polymerides by means of suitable combination of ethylenically

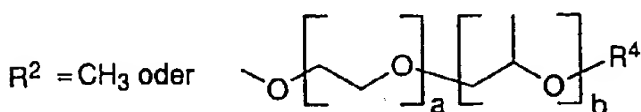
unsaturated monomers at figures of more than 20° C.

Suitable (b) silicon derivatives are the compounds that are known under the INCI names of dimethicone copolyols or silicon tensides, such as, for example, those obtainable under the brand names of Abil (by fa. T. Goldschmidt), Alkasil (by Fa. Rhone-Poulenc), Silicone polyol copolymer (by Fa Genesee), Belsil (byfa. Wacker), Silwet (by Fa. Witco, Greenwich, CT, USA) or Dow Corning they contain compounds with the following CAS numbers: 64365-23-7; 689-54-2; 68938-54-5; 68937-55-3.

Particularly suitable (b) monomers are those that contain the following structural elements:

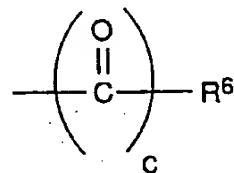
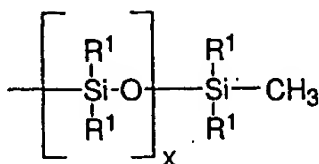


KEY: wobeI = where oder = or.



$R^3 = \text{CH}_3 \text{ oder } R^2$

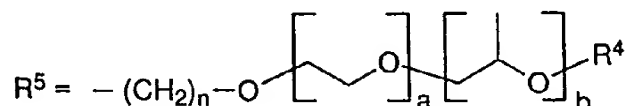
$R^4 = \text{H, CH}_3,$



/11

R^6 signifies an organic residue from 1 to 40 carbon atoms, that can contain amino acid, carboxylic acid, or sulfonate groups, or,

if $c=0$, also the anion of an inorganic acid,
 and where the R^1 residues can be identical or different, and can stem either from the group of aliphatic hydrocarbons with 1 to 20 carbon atoms, cyclic aliphatic hydrocarbons with 3 to 20 C-atoms, being of an aromatic nature or equal to R_5 , where:



with the proviso that at least one of the R^1 , R^2 or R^3 residues is a polyalkyleneoxide-containing residue according to the above-mentioned definition, and that n is a whole number from 1 to 6, x and y are whole numbers in such a way that the molecular weight of the polysiloxane block is between 300 and 30,000, where a and b can be whole numbers between 0 and 50 with the proviso that the sum of a and b is greater than 0, and that C is 0 or 1.

Preferred R^2 and R^5 residues are those where the sum of $a+b$ is between 5 and 30.

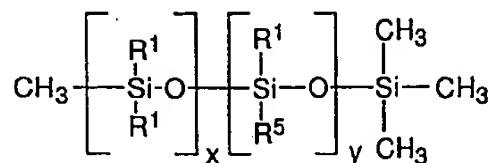
These R^1 groups are preferably selected from the following groups: methyl, ethyl, propyl, butyl, isobutyl, pentyl, isopentyl, hexyl, octyl, decyl, dodecyl and octadecyl, cycloaliphatic residues, especially cyclohexyl, aromatic groups, especially phenyl or naphthyl, mixed aromatic-aliphatic residues,

such as benzyl or phenylethyl as well as tolyl and oxylyl and R^5 .

Particularly suitable R^4 residues are those where - in case of $R^4 = - (CO)_c - R^6$ signifies any random alkyl-, cycloalkyl or aryl residue, that has between 1 and 40 C-atoms and that can carry additional ionogenic groups, such as NH_2 , $COOH$, SO_3H .

When $c=0$, then preferred inorganic R^6 residues are phosphate and sulfate. /12

Particularly preferred (b) silicon derivatives are those having the general structure:



The (b) silicon derivatives as a rule are contained in quantities of 0.1-50, preferably 1-20, particularly preferably 2-15% by weight, in the invention-based polymeride.

Particularly suitable polymers are those that are water-soluble or whose water dispersibility is so great that they are soluble in a solvent mixture of water:ethanol=50:50% by (volume: % by volume) in a quantity of more than 0.1 g/l, preferably more than 0.2 g/l.

If the polymers consist of monomers that carry neutrilizable residues, then one prefers those polymers that are soluble in the neutralized form in a solvent mixture of water:ethanol=50:50 (%)

by volume:% by volume) in a quantity of more than 0.1 g/l, preferably more than 0.2 g/l.

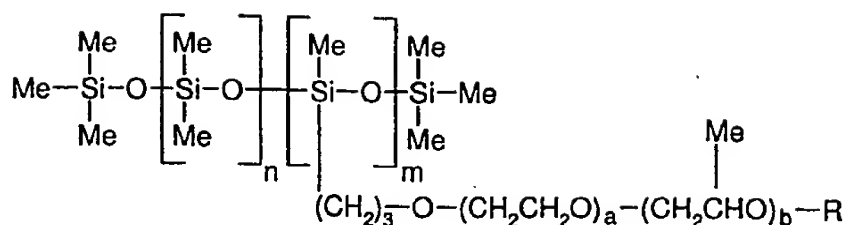
The invention-based polymers are suitable for use as active substances in cosmetic preparations, be it high-grade cosmetic preparations, such as liquid soaps, body lotions, shaving water, facial water, deodorants, and other cosmetic lotions or, above all hair-cosmetic preparations such as hair treatments, hair lotions, hair rinses, hair emulsions, tip fluids, equalizing agents for permanent waves, high-oil treatment preparations, conditioners, strengthening lotions or hair sprays. Depending on the particular field of use, the hair-cosmetic preparations can be applied as spray, foam, gel, gel spray, lotion, or mousse.

The invention-based mixtures can be processed with the aids that are customary for cosmetic preparations, such as, perfume oils, emulsifiers, conservation agents, care substances such as panthenol, collagen vitamins, albumin hydrolysates, stabilizers, pH-value regulators, dyes, solvents, propellant gases, and other customary additives, to produce gels, sprays, lotions, or foams.

Examples

/13

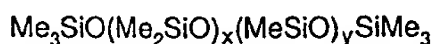
The silicon tensides [surfactants] Wacker Belsil™ DMC 6031 and 6032 can be obtained from Fa. Wacker Chemie GmbH, Munchen and have the following general structure:



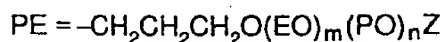
mit R = H, -CO-CH₃

KEY: mit=when

The silicon tensides Silwet™ 7600, 7604 and 7605 can be obtained from Firma Witco Corporation, Greenwich, CT, USA and have the following general structure:



|
PE



Z = Wasserstoff- oder Alkylradikal

KEY: Z=hydrogen or alkylradical

The silicon tenside Dow Corning 190 Surfactant™ can be obtained from Firma Dow Corning Corporation, Midland, MI, USA.

Other (b) silicon derivatives can be made according to the process known to the expert, as described, for instance, in EP 775 717.

Example 1-7

Into a stirred preparation, one drips 50 g of supply 1 and 3.75 g of supply 2. The mixture is then heated to 78° C. After

that, within 1 ½ hour, the rest of supply 1 and supply 2 are dripped in. The mixture is stirred for another 2 hours. After that, supply 3 is dripped in within 15 minutes and one continues stirring for 3 hours at 78° C.

Example 1

Preparation: 175 g ethanol, 7.5 g Dow Corning 190™ /14

Supply 1: 251 g t-butylacrylate, 86 g methacrylic acid, 37 g ethylacrylate, 75 g ethanol

Supply 2: 2 g t-butyl-perpivalate, 100 g ethanol

Supply 3: 1.5 g t-butyl-perpivalate, 57 g ethanol

Example 2

Preparation: 175 g ethanol, 18.75 g Dow Corning 190™

Supply 1: 251 g t-butylacrylate, 86 g methacrylic acid, 37 g ethylacrylate, 75 g ethanol

Supply 2: 2 g t-butyl-perivalate, 100 g ethanol

Supply 3: 1.5 g t-butyl-perpivalate, 57 g ethanol

Example 3

Preparation: 175 g ethanol, 37.5 g Dow Corning 190™

Supply 1: 251 g t-butylacrylate, 86 g methacrylic acid, 37 g ethylacrylate, 75 g ethanol

Supply 2: 2 g t-butyl-perpivalate, 100 g ethanol

Supply 3: 1.5 g t-butyl-perpivalate, 57 g ethanol

Example 4

Preparation: 175 g ethanol, 18,75 g Belsil DMC 6031™

Supply 1: 251 g t-butylacrylate, 86 g methacrylic acid, 37 g ethylacrylate, 75 g ethanol

Supply 2: 2 g t-butyl-perpivalate, 100 g ethanol

Supply 3: 1.5 g t-butyl-perpivalate, 57 g ethanol

Example 6

Preparation 175 g ethanol, 37.5 g Belsil DMC 6032™

Supply 1: 300 g t-butylacrylate, 75 g methacrylic acid, 75 g ethanol

Supply 2: 2 g t-butyl-perpivalate, 100 g ethanol

Supply 3: 1,5 g t-butyl-perpivalate, 57 g ethanol

Example 7

Preparation 175 g ethanol

Supply 1: 251 g t-butylacrylate, 86 g methacrylic acid, 37 g ethylacrylate, 75 g ethanol

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Supply 2: 2 g t-butyl-perpivalate, 100 g ethanol

Supply 3: 1.5 g t-butyl-perpivalate, 57 g ethanol

Example 8

After polymerization, the solution of the polymer from example 7 is mixed with 10% by weight, related to the contained polymer of the silicon derivative Belsil DMC 6032™.

Example 9

40 g Silwet™ L 7604 and 180 g of water were prepared in a stirring unit. While stirring in the nitrogen current, the preparation was heated to 60° C and supply 1 - consisting of 240

g N-vinylpyrrolidione, 267 g 3-methyl-1-vinylimidazoliummethylsulfate-solution (45%) and 0.4 g mercaptoethanol, as well as supply 2, consisting of 2,2' azobis (2-amidinopropane) dihydrochlorid and 70 ml of water - were dosed in within a period of 6 hours. . Then stirring was continued for 2 hours at 60° C and the preparation was diluted with 200 g of water. This resulted in a clear, yellowish polymer solution with a solid content of 41.7% and a K-value of 39 (1% in 0.5 NaCl).

Example 10

40 g Silwet™ L 7604 and 300 ml of water were prepared in a stirring unit. While stirring in a nitrogen current, the preparation was heated to 65° C and supply 1, consisting of 220 g N-vinylpyrrolidione and 333 g 3-methyl-1-vinylimidazoliumchloride solution (60%) and supply 2, consisting of 6 g 2,2'-Azobis (2-amidinopropane)dihydrochloride and 70 ml of water, were dosed in over a period of 6 hours. After that, stirring was continued for 2 hours and the substance was diluted with 100 g of water. This resulted in a clear, yellowish polymer solution with a solid content of 43.0% and a K-value of 44 (1% in 0.5 m NaCl).

Example 11

24 g Silwet™ L 7604 and 200 ml of water were prepared in a stirring unit. While stirring in the nitrogen current, the preparation was heated to 65° C and supply 1, consisting of 160 g N-vinylpyrrolidione, 80 g methacryloxyethyl-N-dimethyl-N-

ethylammonium-ethylsulfate and 300 g of water, as well as supply 2, consisting of 1,3 g 2,2'-azobis-(2-amidinopropane) dihydrochloride and 100 g of water, was dosed in over a period of 6 hours. Stirring was continued for another 2 hours and the substance was diluted with 300 g of water. This resulted in a clear, yellowish polymer solution with a solid content of 22.4% and a K-value of 85 (1% in 0.5 m NaCl). /16

Examples 12 and 13 .

In a mixture of 1.4 g mercaptoethanol, 5.8 g of a polyacrylic acid (obtainable under the trade name Sokalan PA 110 S, from Firma BASF-AG), one suspends 306 g N-t-butyl-acrylamide, 234 g ethylacrylate, 60 g acrylic acid and 60 g of dimethiconcopolyols. After heating to 75° C, one adds 1.2 g t-butyl-peroctoate to the resultant suspension. After 30 or 45 minutes, one adds an additional gram of t-butyl-peroctoate. After the following time tables, one adds additional initiator: 1 hour: 1 gram at 80° C; 1.5 hour: 1 gram; 2 hours: 1 gram at 90° C; 3 hours: 2.7 g; after 4.5 and 6 hours, one gram, each. After that, one repolymerizes for another hour.

The following were used as dimethiconpolyoles:

Example 12: Wacker Belsil DMC 6031

Example 13a: Wacker Belsil DMC 6032

Example 13b: Witco Silwet L-7500

Example 14(Comparison example)

In a mixture consisting of 1.4 g mercaptoethanol, 5.8 g of a polyacrylic acid (obtainable under the trade name Sokalan PA 110 S from Firma BASF-AG), one suspends 306 g N-t-butyl-acrylamide, 234 g ethylacrylate and 60 g acrylic acid. To the resultant suspension, one adds 1.2 g t-butyl-peroxoate after heating to 75° C. After 30 or 45 minutes, one adds an additional gram, each, of t-butyl-peroxoate. After the following time intervals, one adds additional initiator: 1 hour: 1 gram at 80° C; 1.5 hour: 1 gram; 2 hours: 1 gram at 90° C; 3 hours: 2.7 grams; after 4.5 and 6 hours, 1 gram, each. After this, one repolymerizes for another hour.

Example 15

A mixture of 744 g of water, 0.25 g sodium laurylsulfate and 70 g of supply 1 is heated to 40° C. Then one adds 16 g of a 7% aqueous sodium-persulfate solution. Then one heats the mixture to 80° C and one doses supply 1 in over a period of 2 hours. After that one adds 178 g of water and one repolymerizes for 2 hours at 80° C.

Supply 1: 300 g of water

2 g sodium-laurylsulfate

15.7 g silicon copolyol (silwet L7605)

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470 g tert. Butylacrylate

70 g ethylacrylate

161 g methacrylic acid
3 g ethyl-hexylthioglycolate

Example 16

The mixture of 744 g of water, 0.25 g sodium laurylsulfate and 70 g supply 1 is heated to 40° C. Then one adds 16 g of a 7% aqueous sodium-persulfate solution. After that, the mixture is heated to 80° C and supply 1 is dosed in over a period of 2 hours. Following this, one adds 178 g of water and one repolymerizes for 2 hours at 80° C.

Supply 1: 300 g water

2 g sodium laurylsulfate
15.7 g PEO (20)-sorbitan monooleate
422 g tert. Butylacrylate
63 g ethylacrylate
145 g methacrylic acid
3 g ethyl-hexylthioglycolate
70 g silicon copolyol (Silwet™ L7605)

Example 17

A mixture of 744 g of water, 0.25 g sodium-laurylsulfat and 70 g of supply 1 is heated to 40° C. Then one adds 16 g of a 7% aqueous solution of sodium persulfate solution. After that, the mixture is heated to 80° C and supply 1 is dosed in over a period of 2 hours. Following this, one adds 178 g of water and one

repolymerizes for 2 hours at 80° C.

Supply 1: 300 g water

2 g sodium laurylsulfate

15.7 g silicon copolyol (Silwet™ L7600)

470 g tert. Butylacrylate

70 g ethylacrylate

161 g methacrylic acid

3 g ethyl-hexylthioglycolate

Example 18

A mixture of 744 g of water, 0.25 of sodium laurylsulfate and 70 g of supply 1 is heated to 40° C. Then one adds 16 g of a 7% aqueous sodium-persulfate solution. After that, the mixture is heated to 80° C and supply 1 is dosed in over a period of 2 hours. Then one adds 178 g of water and one repolymerizes for 2 hours at 80° C. /18

Supply 1: 300 g water

2 g sodium-laurylsulfate

15.7 g PEO (20)-sorbitan monooleate

422 g tert. Butylacrylate

63 g ethylacrylate

145 g methacrylic acid

3 g ethyl-hexylthiglycolate

70 g silicon copolyol (Silwet™ L7605)

Example 19

A mixture of 744 g of water, 0.25 g of sodium-laurylsulfate and 70 g supply 1 is heated to 40° C. Then one adds 16 g of a 7% aqueous sodium-persulfate solution. After that, the mixture is heated to 80° C and supply 1 is dosed in for 2 hours. Following that, one adds 178 g of water and one repolymerizes for 2 hours at 80° C.

Supply 1: 300 g water

2 g sodium-laurylsulfate

15.7 g PEO (20)-sorbitan monooleate

422 g tert. Butylacrylate

63 g ethylacrylate

145 g methacrylic acid

3 g ethyl-hexylthioglycolate

70 g silicon copolyol (Silwet™ L7600)

Example 20 (comparison example)

A mixture of 744 g of water, 0.25 g of sodium-laurylsulfate and 70 g supply 1 is heated to 40° C. Then one adds 16 g of a 7% aqueous sodium-persulfate solution. After that, the mixture is heated to 80° C and supply 1 is dosed in for 2 hours. Following that, one adds 178 g of water and one repolymerizes for 2 hours at 80° C.

Supply 1: 300 g water

A mixture of 744 g of water, 0.25 g of sodium-laurylsulfate and 70 g supply 1 is heated to 40° C. Then one adds 16 g of a 7% aqueous sodium-persulfate solution. After that, the mixture is heated to 80° C and supply 1 is dosed in for 2 hours. Following that, one adds 178 g of water and one repolymerizes for 2 hours at 80° C.

Supply 1: 300 g water

2 g sodium-laurylsulfate

15.7 g PEO (20)-sorbitan monooleate

422 g tert. Butylacrylate

63 g ethylacrylate

145 g methacrylic acid

3 g ethyl-hexylthioglycolate

70 g silicon copolyol (Silwet™ L7600)

Example 20 (comparison example)

A mixture of 744 g of water, 0.25 g of sodium-laurylsulfate and 70 g supply 1 is heated to 40° C. Then one adds 16 g of a 7% aqueous sodium-persulfate solution. After that, the mixture is heated to 80° C and supply 1 is dosed in for 2 hours. Following that, one adds 178 g of water and one repolymerizes for 2 hours at 80° C.

Supply 1: 300 g water

2 g sodium-laurylsulfate

15.7 g PEO (20)-sorbitan monooleate (Tween 80)

470 g tert. Butylacrylate

70 g ethylacrylate

161 g methacrylic acid

3 g ethyl-hexylthioglycolate

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Example 21

A mixture of 100 g of vinylcaprolactam, 100 g ethanol, 100 g dimethixoncopolyol (Wacker Belsil™ DMC 6031) and 0.75 g t-butylperpivalate is heated to 70° C in a closed boiler that is flushed with nitrogen. After that, one doses in supply 1 over a period of 3 hours and supply 2 over a period of 4 hours. After the end of supply 1, one repolymerizes for 1 hour. Then one adds supply 3 and one heats up to 130° C under pressure. One repolymerizes for 10 hours at 130° C and one cools down.

Supply 1: 800 g vinylcaprolactam

347 g ethanol

Supply 2: 1.5 g t-butylperpivalate

100 g ethanol

Supply 3: 5 g di-t-butylperoxide

187 g ethanol

Example 21

A mixture of 100 g of vinylcaprolactam, 100 g ethanol, 100 g dimethixoncopolyol (Wacker Belsil™ DMC 6032) and 0.75 g t-

butylperpivalate is heated to 70° C in a closed boiler that is flushed with nitrogen. After that, one doses in supply 1 over a period of 3 hours and supply 2 over a period of 4 hours. After the end of supply 1, one repolymerizes for 1 hour. Then one adds supply 3 and one heats up to 130° C under pressure. One repolymerizes for 10 hours at 130° C and one cools down.

Supply 1: 800 g vinylcaprolactam

347 g ethanol

Supply 2: 1.5 g t-butylperpivalate

100 g ethanol

Supply 3: 5 g di-t-butylperoxide

187 g ethanol

Example 23 (comparison example)

A mixture consisting of 100 g vinylcaprolactam, 100 g ethanol and 0.75 t-butylperpivalate is heated to 70° C in a closed boiler that is flushed with nitrogen. After that, one doses in supply 1 over a period of 3 hours and supply 2 over a period of 4 hours. After the end of supply 1, one repolymerizes for 1 hour. Then one adds supply 3 and one heats up to 130° C under pressure. One repolymerizes for 10 hours at 130° C and one cools down.

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Supply 1: 800 g vinylcaprolactam

347 g ethanol

Supply 2: 1.5 g t-butylperpivalate

100 g ethanol

Supply 3: 5 g di-t-butylperoxide

187 g ethanol

Example 24

The polymer solution from example 23 was mixed, after polymerization, with 10% by weight of a silicon tenside (Wacker Belsil™ DMC 6032).

Films of the polymers from the examples were made by spreading the solutions or dispersions of the polymers on glass plates. On these films, we determined the transparency as well as the surface roughness and the friction behavior of the polymer films (see Table 1).

It was found that all invention-based films are transparent and have a particularly smooth surface with little friction resistance.

Films from comparison example 7 are also transparent but display a rougher surface and above all also a very much higher friction resistance. The same poor friction behavior as in the films from examples 8, 14, 20, 23, and 24 was found. Films made in a similar manner from the mixtures of examples 8 and 24 display extremely high stickiness. The films are very soft and are therefore unsuitable use as film forming agents.

Tests of polymers 1-24, in terms of their suitability as hair treatment agents, display corresponding results (table 1).

For this purpose, hair tresses are sprayed with a defined quantity consisting of a standard formulation (2% by weight of the polymer, 40% dimethylether, 58% ethanol). After the hair tresses have been dried, one judges the compatibility and the hold on these hair strands. The invention-based polymerides, made in the presence of silicon surfactants, yield a definitely better hold for the treated hair strands than those hair strands that were treated with comparison polymers 7, 14, 20, and 23.

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Table 1

Bei- spiel	Glätte des Films	Transparenz	Kämmbarkeit	Griff
1	0	+	0	0
2	+	+	+	-
3	+	+	+	0
4	+	+	+	0
5	++	+	++	++
6	+	+	++	0
7	--	+	-	--
8	--	0	-*	-*
12	+	+	++	++
13a	+	+	++	+
13b	+	+	++	+
14	-	+	++	0
21	+	+	+	+
22	+	+	++	+
23	-	+	0	-
24	--	-	-*	-*

KEY: 1- example; 2- smoothness of film; 3- transparency; 4- compatibility; 5- hold

* a test on hair tresses was not made on account of the fact that the stickiness was much too high.

The entries in the Table have the following meaning:

- ++ = Very good performance
- + = Good performance
- 0 = Satisfactory performance
- = Unsatisfactory performance
- - = Inadequate

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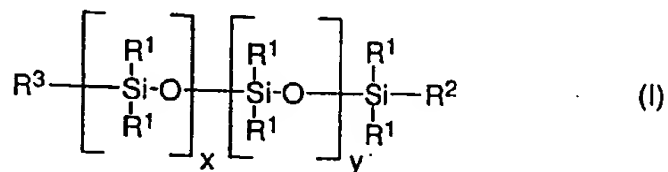
CLAIMS

1. Use of polymers, that are water-soluble or water-dispersable or that - if they consist of monomers with neutrilizable residues - are water-soluble or water-dispersable in the neutralized form, which are obtained in that one radically polymerizes.

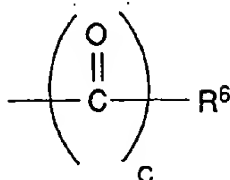
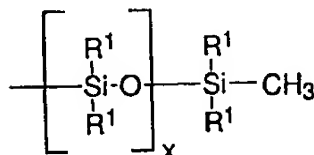
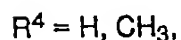
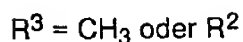
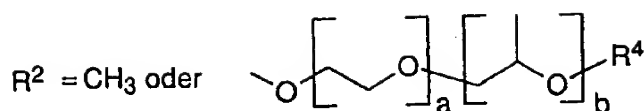
(a) Ethynically unsaturated monomers in the presence of

(b) polyalkyleneoxide-containing silicon derivatives,
for cosmetic formulations.

2. Use according to Claim 1, characterized in that, as polyalkyleneoxide-containing (b) silicon derivatives one uses those that have formula I.

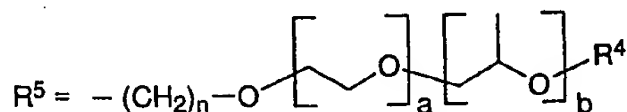


KEY: wobe= where; oder = or



R^6 signifies an organic residue consisting of 1 to 40 carbon atoms, that can contain amino acids, carboxylic acids, or sulfonate groups, or, if $c=0$, also signifies the anion of an inorganic acid and where the R^1 residues can be identical or different, and stem either from the group of aliphatic hydrocarbons with 1 to 20 carbon atoms, are cyclic aliphatic hydrocarbons with 3 to 20 C-atoms, have an aromatic nature or are equal to R^5 , where:

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with the proviso that at least one of the R^1 , R^2 or R^3 residues is a polyalkyleneoxide-containing residue according to the above

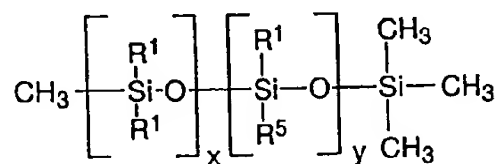
mentioned definition,

and where n is a whole number from 1 to 6,

x and y are whole numbers in such a way that the molecular weight of the polysiloxane bloc is between 300 and 30,000,

where, a, b can be whole numbers between 0 and 50, with the proviso that the sum of a and b is greater than 0, and that c is 0 or 1.

3. Use according to Claim 2, characterized in that formula I has the following meaning:



4. Use according to Claim 1, characterized in that the quantitative ratios are:

- (a) 50-99.9% by weight and
- (b) 0.1-50% by weight.

5. Use according to Claims 1 to 4 as hair care agent.